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(54) **Photographic materials comprising microprecipitated dye dispersions suitable for rapid processing applications**

(57) A photographic material is disclosed comprising a support and on at least one side thereof at least one light-sensitive silver halide emulsion layer characterised in that said material comprises at least one hydrophilic colloid layer, comprising a dispersion of at least two dyes: at least one dye being a merostyryl dye and the at least one other dye being an oxonol dye, wherein both dyes are soluble at a pH value above 8.0 and insoluble at a pH value below 6.0, and wherein at least said oxonol dye is in the form of a microprecipitated dispersion. Preparation methods of said dispersions are disclosed as well as a method of processing said photographic material, said method comprising the steps of developing, fixing, rinsing and drying, within a total processing cycle of less than 60 seconds.

EP 0 724 191 A1

Description

1. Field of the invention.

5 The present invention relates to dispersions of filter dyes and their use as antihalation and anti-cross-over dyes in photographic elements.

2. Background of the Invention

10 Dispersions of non-spectrally sensitizing dyes are widely used in photographic elements, particularly in photographic elements of the silver halide type. They may be used in a photosensitive silver halide emulsion layer as screening dye dispersions, in an undercoat layer adjacent to the photosensitive layer and/or in a backing layer on the side of the support opposite to the photosensitive layer(s) in order to absorb reflected and scattered light thereby serving as antihalation dye dispersions. In an overcoat or interlayer the said dispersions may be used to shield a particular photo-
 15 sensitive layer against undesired exposure being therefore referred to as filter or absorber dye, thereby adjusting the sensitivity of a photographic element as required in the production specifications.

For example in order to improve image sharpness an absorber dye dispersion can be present in one or more filter layers between silver halide emulsion layers that are coated at opposite sides of a transparent film support of an X-ray recording material. The imagewise exposure of said recording material proceeds in a cassette between a pair of X-ray
 20 intensifying screens that each are held in contact with an adjacent silver halide emulsion layer. By said arrangement the imaging light that would cross the support and to some extent becomes scattered thereby, is considerably attenuated and cannot give rise to an unsharp image in an opposite silver halide emulsion layer.

The absorption spectrum of the dye dispersion should approximately be equal to the sensitivity spectrum of the corresponding silver halide emulsion in the layer of which a sharp image has to be reproduced.

25 On the one hand it is very important that filter dyes present in dispersed form remain, i.e., that they are non-migratory, in the layer wherein they have been incorporated especially when this layer is in direct contact with the silver halide emulsion layer in order to prevent a desensitizing action on the silver halide. On the other hand the filter dyes present in dispersed form may not stain the photographic material after image processing. Therefore preference is given to filter dyes that decolorize or can be removed from the photographic element in the processing stage. This requirement is
 30 nowadays becoming more and more stringent as rapid processing times are of increasing interest.

As described in US-P 3,560,214 dyes comprising a carboxyl and phenyl substituted pyrazoline nucleus linked through a methine group to a dialkylaminophenyl group can be removed relatively easily in alkaline aqueous processing liquids.

Other filter dyes characterized by the presence of a 2-pyrazoline-5-one nucleus substituted with a carboxyphenyl group and including a methine group or chain linked to a dialkylamino group are described in US-P 4,857,446. The decolorization of said filter dyes proceeds very rapidly in alkaline aqueous processing baths. The monomethine dyes have an absorption spectrum of which the maximum is in the shorter wavelength range of the visible spectrum so that normally a second filter dye is needed to block or absorb green light and even a third one to absorb radiations of longer wavelengths, e.g., radiations in the red or even in the infrared region. In many applications an absorption of radiation in
 40 the whole visible wavelength range of 400 to 700 nm is required and even an absorption from ca. 370 nm, lying in the wavelength range of the maximum absorption value of non-spectrally sensitised silver halides, is still more required.

Once a filter dye has been selected, the problem is how to get the filter dye in a coated layer so that all the requirements mentioned previously are met.

One of the possibilities is to make use of solid particle dispersions of water insoluble dyes as has been described
 45 in EP 0,384,633 A2; EP 0,323,729 A2; EP 0,274,723 B1, EP 0,276,566 B1, EP 0,351,593 A2 and US-Patents 4,900,653; 4,904,565; 4,949,654; 4,940,654; 4,948,717; 4,988,611 and 4,803,150.

Normally storage dispersions of said solid particle dispersions are formed in aqueous gelatinous medium by means of ball milling, sand milling, roller milling and other techniques. Said techniques are not very economically interesting as milling times from 6 to 24 hours are not exceptional. The mechanical load therein is very hard as temperature
 50 increases may lead to a partial destruction of the dyes. Especially when a gelatinous dispersion is made from a mixture of dyes, necessary to get the desired absorption wavelength spectrum, milling techniques are leading to the blocking of the mechanical process as the viscosity is increasing dramatically. Moreover the long preparation time makes a preparation "directly ready-for-incorporation in coating solutions" impossible. The dispersions have to be stored and desintegration of the dispersing colloid and/or agglomeration of the dye particles may occur.

55 To avoid the mechanical load during the preparation of the dispersions as has been described hereinbefore attempts have been made to provide dispersions of dyes by means of the so called "microprecipitation technique". Microprecipitation techniques have, e.g., been described in DE-PS 932 343 wherein the statement is made that "alkaline soluble dyes can be precipitated in acid medium, e.g., in the presence of gelatin" and in EP-Specification 15 601, wherein it has been disclosed that "it is possible to use the dyes in their salt form and to convert them in situ into their

acid form". Further prior art concerning this topic can be found in JP-A 61185568, in EP-S 19 299, EP-A's 323 729; 549 486 and 549 489; in GB 1,210,253 and 1,305,441 and in US-P's 4,970,139; 5,075,205; 5,077,184; 5,089,380; 5,104,776; 5,155,015 and in 5,182,189.

Precipitation of mixtures of dyes in an alkaline gelatinous solution of alkaline soluble dyes by acidifying said solution, in order to get them in dispersed form, covering an extended wavelength region, can however lead to an increase of the viscosity of the solution. This depends not only on the degree of viscosity of the gelatin used, but also on the choice of the dye mixture (amount of dyes and ratio by weight of the dyes), the particle size (further determining the dissolution rate) and of the chemical composition of the dyes.

It may be concluded that nowadays from the viewpoint of non-diffusibility, rapid decolourizing or removal by rapid processing and stability the requirement is very severe to have suitable dyes incorporated in the layers of silver halide photographic materials. The said high stability in the photographic material is thereby required not only under the influence of the ingredients present in the emulsion layers prior to coating, but especially under severe storage conditions of the packed material, e.g., under circumstances of high temperatures and high degrees of humidity.

3. Objects of the Invention

It is an object of the present invention to provide dye dispersions of mixtures of dyes having acceptable viscosities from which the dyes can be incorporated easily in non-migratory state in hydrophilic colloid layers of photographic materials wherefrom they can be rapidly removed in alkaline aqueous liquids used in the processing of said materials.

More specifically it is an object to provide dispersions of dyes for incorporation in a hydrophilic layer of a silver halide photographic material in order to absorb radiation in the wavelength region between 370 and 700 nm and to provide a sufficient absorption density for low coating amounts of dyes.

It is a further object of the present invention to provide dye dispersions of mixtures of dyes having high density in the said spectral region, thereby reducing the cross-over effect in double-side coated photographic elements, particularly radiographic materials, or providing good image quality by suitable antihalation operation in single-side coated materials as, e.g., some specific radiographic materials (for mammography etc.), hardcopy materials or materials for micrography.

A still further object of this invention is to eliminate the need to provide storage dispersions and to prepare these dispersions "in situ" at the time the coating solution is prepared.

Other objects will become apparent from the description hereinafter.

4. Summary of the Invention

In accordance with this invention a photographic material is provided comprising a support and on at least side thereof at least one light-sensitive silver halide emulsion layer characterised in that said material comprises at least one hydrophilic colloid layer, comprising a dispersion of at least two dyes: at least one dye being a merostyryl dye and the at least one other dye being an oxonol dye, wherein both dyes are soluble at a pH value above 8.0 and insoluble at a pH value below 6.0, and wherein at least said oxonol dye is in the form of a microprecipitated dispersion. The choice if this pH range is related with the prior art wherefrom it is known that in the presence of one or more anionic, weakly acidic groups in the dyes, important to provide sufficient non-migratory character at coating pH values, the said pH range is situated in the range from 4 to 8.

A method of preparing the dispersion of at least two dyes according to this invention is also disclosed, wherein at least said at least one oxonol dye is microprecipitated by acidifying an aqueous alkaline solution.

Further a method of processing the photographic material is disclosed, comprising the steps of developing, fixing, rinsing and drying, within a total processing cycle of less than 60 seconds.

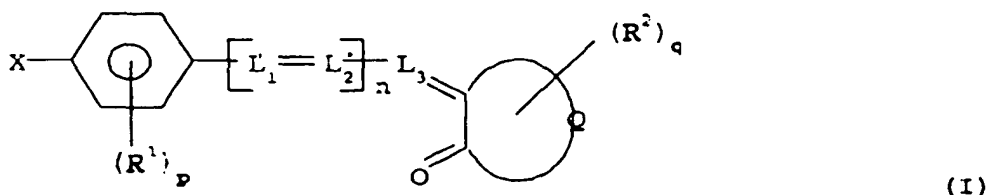
5. Detailed description of the Invention

In the context of this invention the term "dispersion of at least two dyes" has to be interpreted as being different from a mixture of two classical dispersions obtained by mechanical techniques such as, e.g., ball milling said dyes apart or together in the presence of gelatin.

According to this invention, it is an essential feature of the dispersion of at least two dyes present in a silver halide material according to this invention that at least one oxonol dye is present in the form of a microprecipitated dispersion. Said microprecipitated dispersion is obtained by the method of acidifying an aqueous alkaline solution. The presence of the at least one merostyryl dye in microprecipitated form may occur in the said dispersion mixture.

Dye dispersions of at least two dyes to be incorporated in the silver halide photographic material according to this invention are those wherein at least one merostyryl dye corresponding to the formula (I), and at least one microprecipitated oxonol dye corresponding to the formula (II), are present.

Preferred merostyryl dyes present in at least one hydrophilic layer of a photographic material according to this invention are represented by the general formula (I)



15 wherein

n represents 0 or 1;

each of p and q independently represents 0, 1 or 2;

Q represents the atoms necessary to form an acidic nucleus;

20 each of R^1 and R^2 independently represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, COOR^3 , NHCOR^4 or NHSO_2R^5 with R^3 representing hydrogen or substituted or unsubstituted alkyl, each of R^4 and R^5 independently representing substituted or unsubstituted alkyl, or substituted or unsubstituted aryl,

X represents OR^6 , SR^6 or NR^7R^8 , wherein

R^6 represents H, substituted or unsubstituted alkyl, substituted or unsubstituted aryl and

25 each of R^7 and R^8 which may be the same or different represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl or the necessary atoms to form a ring together with the N-atom to which they are attached and the C-atom of the phenylene ring in ortho position with respect to said N-atom; R^7 and R^8 together may also represent the necessary atoms to form a ring with the N-atom to which they are attached;

L_1 , L_2 , L_3 represent substituted or unsubstituted methine with the proviso that, if substituted, at least one of L_1 , L_2 or L_3 must be substituted by $-\text{CONR}^9\text{R}^{10}$; $-\text{CON}(\text{R}^{11})-$; $-\text{COOR}^9$; $-\text{CN}$;

30 R^9 and R^{10} which may be the same or different represent hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl,

R^{11} represents atoms to form a ring with an atom of Q , defined hereinbefore;

and wherein at least one of R^1 to R^{11} contains an ionizable group.

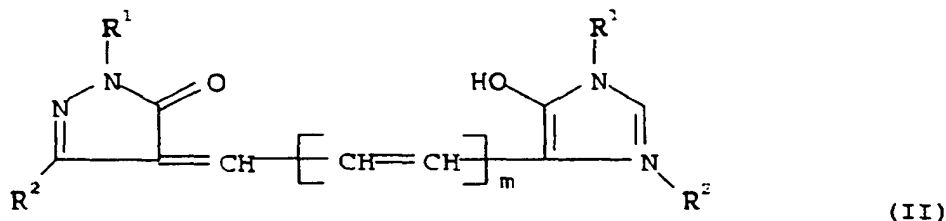
Preferably said ionizable group is situated at R^2 .

35 In formula (I) of the said merostyryl dye the acidic nucleus is preferably a pyrazolone, barbituric acid, thiobarbituric acid, rhodanine, hydantoin, oxazolidindione, thio-oxazolidindione or an isoxazolinone.

In a further preferred embodiment in formula (I) of the said merostyryl dye, the necessary atoms represented by L_1 - L_3 are mono- or trimethine.

40 Dyes according to the general formula (I) have been described in EP-A's 586 748; 587 230; US-P 5,344,749 and in EP-Application No. 93203382, filed December 2, 1993.

A preferred oxonol dye which is, according to this invention, present in the form of a microprecipitated dispersion is represented by the general formula (II)



55 wherein

$m = 0, 1$ or 2 ;

each of R^1 and R^2 has the same meaning as given in formula (I),

and at least one of R^1 and R^2 in formula (II) has an ionizable group.

In a preferred embodiment in the formula (II) of the said oxonol dye $m=2$, $R^1=p$ -carboxyphenyl and $R^2=CH_3$.

Said oxonol dye(s) has (have) been described, e.g., in US-P's 4,092,168 and 4,288,534.

According to this invention, it is specifically contemplated that the dispersion of at least two dyes is incorporated in at least one hydrophilic colloid layer of a silver halide photographic material wherein the absorption spectrum is in the region from 370 to 700 nm and wherein the amount per sq.m. of the merostyryl dye(s) corresponding to the formula (I) is from 0.1 to 0.3 g, whereas the amount per sq.m. of the oxonol dye(s) is about 0.1 g, i.e. from 0.09 to 0.11 g.

In a preferred embodiment the ratio by weight, of the said at least one merostyryl dye corresponding to the formula (I) and the said at least one oxonol dye corresponding to the formula (II) is from 3:1 to 1:1 in the said at least one hydrophilic colloid layer of the silver halide photographic material according to this invention.

Preparation methods of the dye dispersion of the said at least two dyes, according to this invention described hereinafter, are leading to particle sizes of the dispersion which are smaller than 500 nm. Particle sizes smaller than 500 nm require an acidifying step of alkaline solutions (coating solutions or separate solutions containing at least one dye) in well-defined pH-conditions. A pH-stat apparatus can be used to control these conditions, but the rate at which the acidic solutions are added is important too. Both conditions are not only determining the ultimate particle size of the dispersed dye particles, but are also determining the absorption densities over the whole wavelength region from 370 to 700 nm that can be obtained. Preferred absorption densities in said wavelength region are at least 0.3, and, more preferably, at least 0.6. It is evident that more finely dispersed dye particles require a lower coating amount of the said dyes in order to reach the preferred absorption densities. Moreover in the alkaline developer it is evident that finer alkali soluble dye particles are decolourised more quickly and can be more easily removed from the silver halide photographic material in the further processing steps. It is clear that this is in favour of rapid processing applications of the photographic material according to this invention.

A preferred acidic solution to acidify alkaline dye solutions and/or coating solutions is citric acid, although other acids can also be used.

In a preferred embodiment microprecipitation of an alkaline dye solution proceeds in the presence of a protective colloid. Preferred protective colloids are gelatin and/or silica sol. Further specific embodiments if silica sol is used as a protective colloid have been described in EP-A 569 074, which is incorporated herein by reference. In the thus obtained dye dispersions the ratio by weight of gelatin or silica to the dyes is preferably from 1:5 to 5:1.

One method of incorporating dyes in at least one hydrophilic colloid layer of a photographic material according to this invention consists in that at least one oxonol dye according to the general formula (II) is microprecipitated by the step of acidifying an alkaline solution in which said at least one dye is soluble. Said alkaline solution can be a separately prepared solution that is added to the coating solution afterwards. After addition of (a) merostyryl dye(s) according to the general formula (I) to the said coating solution coating is performed on at least one side of a support to form at least one hydrophilic colloid layer of said photographic material.

In another embodiment at least one oxonol dye according to the general formula (II) is microprecipitated by acidifying the coating solution which already contains a merostyryl dye according to the general formula (I) in dispersed form. Said coating solution can be acidic or alkaline beforehand. The at least one merostyryl dye according to the general formula (I) can be present as a microprecipitated dispersion (when the coating solution is acidic) or as a solubilized dye (when said coating solution is alkaline).

Another method of incorporating dyes in at least one hydrophilic colloid layer of a photographic material according to this invention consists in that said at least one oxonol dye according to the general formula (II) is microprecipitated before addition to the acidic coating solution which contains the merostyryl dye according to the general formula (I) in dispersed form and wherein said microprecipitated oxonol dye is added thereto. In this case the coating solution is already acidic. Further coating of the said coating solution follows on at least one side of a support to form at least one hydrophilic colloid layer.

In another embodiment, an alkaline solution of the at least one oxonol dye according to the general formula (II) is added to the acidic coating solution, which contains the merostyryl dye according to the general formula (I) in dispersed form.

In a further embodiment said merostyryl dye(s) according to the formula (I), present in dispersed form, has (have) been prepared by the step of microprecipitation, characterised in that an aqueous alkaline solution of the said dye(s) is (are) acidified. This preparation step can occur in the coating solution before addition of the oxonol dye(s) or in a separate precipitation vessel.

In still another embodiment incorporating dyes in at least one hydrophilic colloid layer of a photographic material according to this invention is performed in such a way that at least one merostyryl dye according to the general formula (I) and at least one oxonol dye according to the general formula (II) are microprecipitated apart or together before or after addition to the coating solution by acidifying the said at least one aqueous alkaline dye or alkaline coating solution. This addition to the coating solution may proceed consecutively or simultaneously. Said coating solution may still be alkaline, whereafter an acidifying step can be applied afterwards.

Irrespective of the fact in what form the merostyryl dye(s) are present in the coating solution comprising a mixture of dyes according to this invention, the coating solution can be acidified just before coating on a support. For that pur-

pose an acidic solution can be added to the coating solution or an acidic coating solution can be coated simultaneously together with the said coating solution. Said coating solution can be alkaline or slightly acidic before coating.

Although the presence of dispersions of dyes according to this invention in the light-sensitive silver halide layer(s) is not excluded, it is preferred to incorporate them into hydrophilic non light-sensitive layers as there are one or more backing layers in the case of single side coated materials, antihalation undercoat layers, interlayers, protective layers and/or outermost layers.

Further ingredients used in the dye containing as well as in the other layers of the photographic material according to this invention have recently been described in Research Disclosure 36544, september 1994, p. 501-541, which is incorporated herein by reference.

In a preferred embodiment according to this invention an X-ray photographic material or a material for micrography contains one or more layers wherein dye dispersions as described hereinbefore are incorporated, although other materials are not excluded either.

Also multilayer materials such as, e.g., colour materials, may contain at least one filter layer, interlayer and/or antihalation layer wherein dye dispersions prepared according to the method of this invention are present. Interlayers in the layer arrangement of such multilayer materials may contain very fine light-insensitive silver halide particles with a diameter of 10 to 100 nm known as Lippmann emulsions, incorporated into said layers, e.g., to serve as scavengers to prevent oxidized developer products to migrate into adjacent layers. In an outermost layer or layers or in an emulsion layer or layers the dye dispersions prepared by the method according to this invention may be used to adjust the sensitivity of the photographic material as required by the production specifications. So it is possible to apply a dosing feeder just before coating the hydrophilic layer concerned and to control the production of the photographic material in this way.

The dye dispersions according to this invention, absorbing in the blue, green and red spectral range can be used advantageously between silver halide emulsion layers of double-sided emulsion coated (duplitized) photographic film material as applied in X-ray recording for use with visible light emitting X-ray conversion phosphor screens. By said arrangement the light that would cross the support and to some extent become scattered thereby, is considerably attenuated and cannot give rise to an unsharp image into an opposite silver halide emulsion layer.

In a particular embodiment of the present invention the dye dispersions are incorporated into non-light sensitive hydrophilic colloid layers a radiographic material that is provided at both sides of the support with a silver halide emulsion layer and an antistress layer as a protective layer coated thereover. The radiographic material preferably has on both sides of the film support silver halide emulsion coatings that are split into two distinctive emulsion layers having silver halide crystals of different average grain size one of which is a high speed emulsion layer and the other is a low speed emulsion layer; the high speed emulsion layer being situated at a larger distance from the support than the low speed emulsion layer. In this way the sensitometric curve can be fine-tuned, giving the perfect profile required for the specific application. The layer arrangement may also be opposite to the previously cited sequence in order to get a higher contrast. Moreover even without using a separate anticrossover layer this layer arrangement reduces crossover, especially in the critical low density area. In the presence of antihalation undercoat layers preventing crossover, said layers containing the dispersions, according to this invention, the crossover reduction is improved without leaving a colour stain upon processing, especially upon rapid processing in less than 60 seconds, preferably in 45, 38 or 30 seconds as reference processing times of materials with high-throughput.

All combinations of symmetrically double-sized film materials with a symmetric or asymmetric set of intensifying screens or combinations of double-sized films with asymmetric emulsion layers, whether or not duplitized, in combination with a symmetric or asymmetric set of intensifying screens can be useful, depending on the specific needs.

According to another embodiment said dispersions absorbing blue, green and red light can be used in an antihalation layer of a photographic silver halide photographic material according to this invention in order to improve image sharpness by absorbing exposure light penetrating the emulsion layer(s) into the direction of the support. The use of said light absorbing dye dispersions in an antihalation layer is particularly advantageous in silver halide photographic emulsion materials that are made spectrally sensitive to blue, green or red light and of which the exposure proceeds with a suitable light source.

Further a method of processing is disclosed of a photographic material according to this invention built up with hydrophilic layers containing dye dispersions according to this invention, said method comprising the steps of developing, fixing, rinsing and drying, within a total processing cycle of less than 60 seconds.

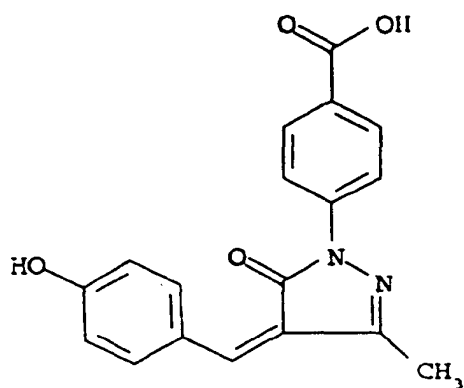
Depending on the particle size of the dispersed dyes, a processing time of less than 45 seconds and even less than 30 seconds can be obtained. At a pH of at least 10 the dyes dispersed as disclosed herein are easily solubilized and are indeed removed almost completely from a hydrophilic waterpermeable colloid layer of a photographic silver halide emulsion material by its common alkaline aqueous liquid processing without leaving any residual stain. The presence of sulfite in the processing solution contributes to a more rapid discoloration of the filter dyes.

The following examples illustrate the present invention and the advantages obtained without however limiting it thereto

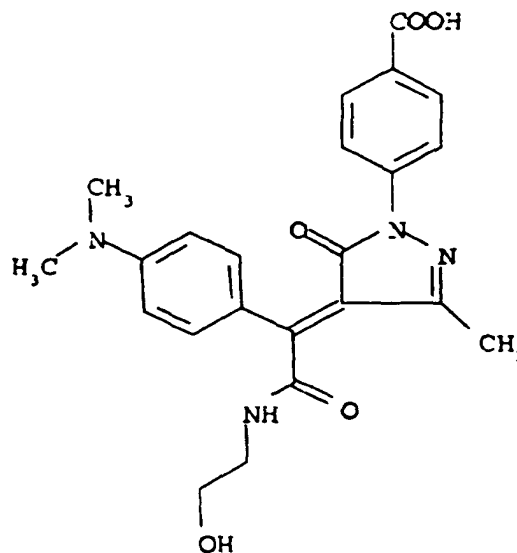
6. EXAMPLES

Formulae of the dyes used in the examples to illustrate the invention are given below.

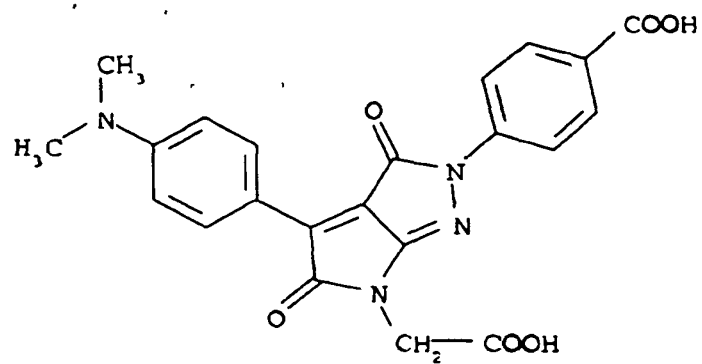
5 A. Merostyryl dyes according to the general formula (I)



(III a)

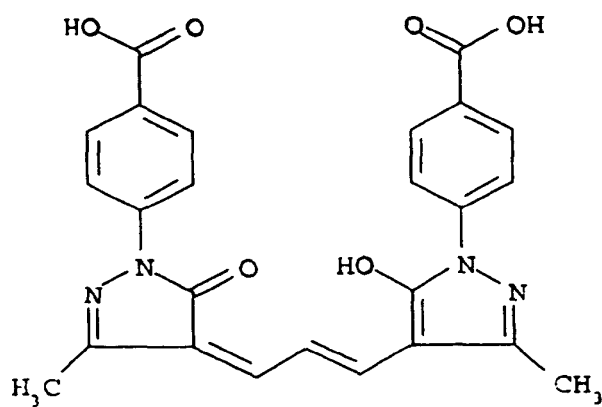


(III b)

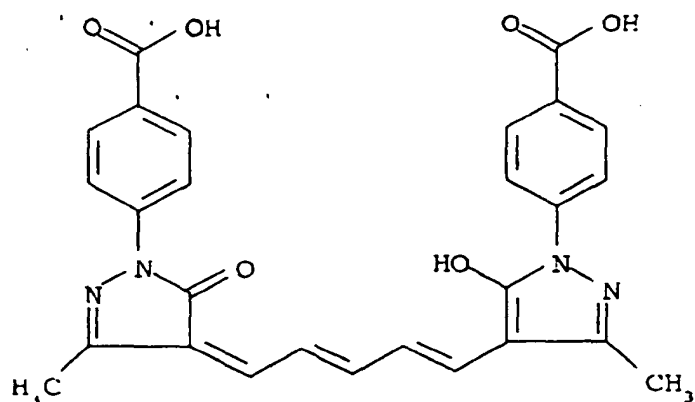


(III c)

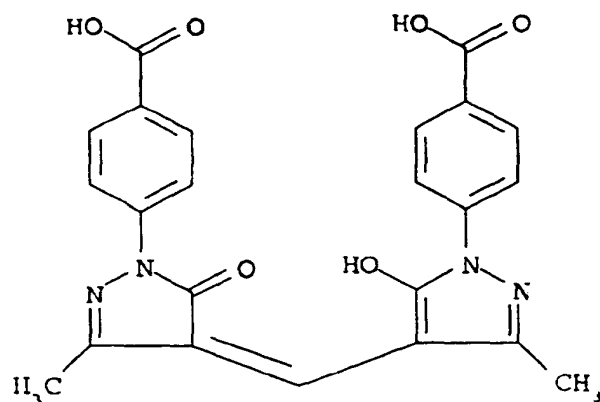
B. Oxonol dyes according to the general formula (II):



(IV a)



(IV b)



(IV c)

Procedure for the preparation of dye dispersions.

Method A.

a. 10 g of filter dye-(IVc) and 4.4 g of filter dye-(IVb) were dispersed at 40°C in 200 g of a 10% aqueous gelatin solution by using a rotating pearl mill containing as a milling material zirconium oxide pearls sizing 0.6 to 0.8 µm. At a dye particle size of about 1 µm the milling process was stopped and the dispersion separated from the milling material.

The dispersion was added to a gelatin solution of 20 % at 40°C, so that the concentration of the dye and of gelatin becomes 4.4 %.

b. Filter dye-(IIIa) was dispersed in the same way as in a.

Method B.

A more convenient method of dispersion is followed by preparing the dispersion "in situ" in a coating solution.

The dyes were dissolved in water and alkali as described hereinafter and were added to a gelatin solution at 40°C. The pH value was adjusted with an aqueous acidic solution to a value of about 5.0 in order to obtain a particle size of less than 500 nm.

5 Method C.

A dispersion was obtained by dissolving dye-(IIIa) and dye-(IVb) in an aqueous alkaline solution. The solutions were added to an aqueous solution of 20 % of gelatin and dispersed by neutralisation with an aqueous acidic solution to a solution pH of about 5.0.

10 A 2 %, respectively 1 % dispersion of the respective dye-(IIIa) and dye-(IVb) in 3.3 % of gelatin was obtained, the particle size of which was less than 500 nm.

Remark: with dye-(IVb) and dye-(IVc) this dispersion preparation method could not be applied because of the very high viscosity obtained during neutralisation.

15 Solutions:

20 g of dye-(IIIa) were dissolved in water containing 4.3 g of NaOH. The total volume was adjusted to 100 ml (the measured pH value was 9.0).

10 g of dye-(IIIb) were dissolved in water containing 1.1 g of NaOH. The total volume was adjusted to 100 ml. A pH of about 9.0 was measured.

1 g of dye-(IVa) was dissolved in water and NaOH was added in order to obtain a solution having a pH value between 7 and 8 and a dye concentration of 1 %.

In the same way the dye-(IVb) and dye-(IVc) were dissolved.

Dye dispersions prepared by acidifying the alkaline solutions of said dyes are called "in situ dispersions" (further indicated by ISD), opposite to the classic "gelatinous milling dispersions" (further indicated as GMD).

Example 1

Coating solutions were made for antihalation layers. Besides the dyes or dye dispersions added thereto, a latex compound, surfactants, a biocid (phenol) and a hardening agent (formaldehyde) were present in the aqueous gelatinous solution.

Mixtures of dispersions were coated and dried on a polyethylene terephthalate film support of 175 μm thickness in order to obtain a dye coverage of 0.1 g/m^2 of dye (IVb) and 0.2-0.3 g of dye (IIIa), a gelatin coverage of 1 g/m^2 and a coverage of hardening agent of 0.016 g/m^2 .

For the one-side coated materials in Figs. 1-3 the absorption wavelength spectrum of the said materials is given as has been measured at a Dianon Corporation Match Scan spectrophotometer with diffuse light:

- Fig. 1 shows the absorption wavelength spectrum of a mixture of 0.1 g/m^2 of the GMD of dye (IVb) and 0.24 g/m^2 of the GMD of dye (IVc) (comparative).
- Fig. 2 shows the absorption wavelength spectrum of a mixture of the alkaline solution of 0.3 g/m^2 of dye (IIIa) and of 0.1 g/m^2 of the alkaline solution of dye (IVb) the mixture of which an ISD is made after the mixed alkaline solution has been added to an acidic coating solution, acidified by the addition of citric acid.
- Fig. 3 shows the absorption wavelength spectrum of a mixture of 0.3 g/m^2 of the GMD of dye (IIIa) and of 0.08 g/m^2 of the ISD of dye (IVb), the mixture of which has been prepared by the addition to a coating solution comprising GMD of dye (IIIa), adding citric acid to get an acidic coating solution and adding afterwards the alkaline solution of dye (IVb).
- Fig. 4 shows the absorption wavelength spectrum of a mixture of 0.08 g/m^2 of the ISD of dye (IVb), prepared by acidifying an alkaline coating solution comprising dye (IVb) by the addition of citric acid and adding thereto 0.3 g/m^2 of the GMD of dye (IIIa).

As can be concluded from these Figures it is clear that in the wavelength region between 370 and 700 nm a relatively uniform absorption density of at least 0.6 is obtained if mixtures of dyes described hereinbefore are added consecutively to the coating solution, wherein from at least one of said dyes, being at least one oxonol dye, a ISD is made.

Example 2

The viscosity of the coating solution of Example 1, as in Fig. 2, was measured at a coating pH of 5.3 and at a coating temperature of 36°C by means of a viscosimeter and expressed in mPas for each measurement.

In Table 1 data of viscosities are given which were measured immediately (0 h.), after 2 (2 h.) and after 4 hours (4 h.) for different amounts (in grams) of the given dyes precipitated "in situ" individually or in a mixture of two dyes in a coating solution having a weight of 1000 grams, comprising 40 grams of gelatin of low viscosity (Rousselot type 13311).

Table 1

dye IIIa (grams)	dye IVb (grams)	dye IVc (grams)	visco 0 h. (mPas)	visco 2 h. (mPas)	visco 4 h. (mPas)
-	2	-	6.0	6.5	7.0
-	4	-	7.0	8.0	8.0
-	6	-	11.0	15.0	16.0
-	-	4.46	4.5	4.5	4.5
-	-	6.69	5.5	5.5	5.5
-	-	8.92	6.0	6.0	6.0
-	2	1.11	5.5	7.0	7.0
-	2	2.23	8.5	11.0	14.0
-	2	3.34	13.0	17.0	20.0*
6.4	2	-	8.0	9.0	9.0
4.8	2	-	4.0	4.5	4.5

* viscosities increase up to a value of 30 mPas at a pH value of 5.0.

As can be seen from Table 1 the values after several hours of the viscosities of the coating solutions of antihalation layers comprising dyes, the dispersions of which has been prepared "in situ" are not exceeding critical values of about 20, even not for higher concentrations of the dyes used in combination with each other. Even for higher concentrations of the merostyryl dye 1, in combination with the oxonol dye (IVb) low viscosities can be measured, whereas for a combination of dye (IVc) with dye (IVb) higher concentrations of dye (IVc) are leading to higher viscosities which are increasing much more rapidly with storage time.

According to this invention, "in situ" prepared dispersions of merostyryl dyes and oxonol dyes are offering the possibility to make "in situ" prepared dispersions, opposite to the little handsome "storage dispersions". Moreover the viscosity of the coating solution is not increased, even not if higher amounts of dyes are precipitated and/or if said coating solution is stored for several hours before coating.

Example 3

In this example the influence of the presence of dye-(IIIa) on the viscosity by dispersing dye-(IVb) was determined. Viscosities were measured for coating solutions comprising 40 g of gelatin per 1000 g wherein use was made of the following types of gelatin:

A: Rousselot type 13311; having a low viscosity.

B: Rousselot type 10985; having a moderate viscosity.

C: Koepff type 7985; having a low viscosity and characterised by the absence of Ca^{2+} .

In Table 2A amounts in grams of dyestuff, added to the 1000 g of coating solution as an alkaline solution of resp. 20%, 4% and 1%, are given, whereas in Table 2B viscosities in mPas are given at 36°C.

Table 2A

Gelatin	A	A	B	B	C	C
dye-IVb	2	2	2	2	2	2
dye-IVc	4.46	0	4.46	0	4.46	0
dye-IIIa	0	6.4	0	6.4	0	6.4

Table 2B

to pH	A	A	B	B	C	C
5.5	60	4.5	120	6.5	123	4.5
5.0	***	4.5	***	6.0	***	4.0
4.5	***	4.5	***	5.5	***	4.0
*** the viscosity cannot be measured as it is too high.						

As can be seen from Table 2B the viscosity is not measurable for a coprecipitated microdispersion made from dye-IVb and dye-IVc.

Example 4

In this Example the influence on the viscosity of a 50 ml coating solution having a pH value varying from 5.5 to 4.5 has been controlled as a function of the coated amount of gelatin and of the ratio by weight of dye IIIa to dye IVb, said dye IIIa and dye IVb being prepared "in situ" after precipitation of alkaline solutions by acidifying them.

Table 3

dye IIIa (g/m ²)	dye IVb (g/m ²)	wt.ratio dye1/dye2	gel. (g/m ²)	visco pH=5.5	visco pH=5.0	visco pH=4.5
0.32	0.10	3.2	2	5.5	5.5	16.5
0.16	0.10	1.6	2	9.0	11.0	43.0
0.08	0.10	0.8	2	12.0	11.0	45.0
0.32	0.20	1.6	2	6.5	6.0	20.0
0.16	0.20	0.8	2	41.0	34.0	**
0.08	0.20	0.4	2	55.0	39.0	**
0.16	0.10	1.6	1	4.0	4.0	12.0
0.16	0.10	1.6	0.5	3.0	3.0	12.0
** very high viscosity; not measurable.						

As can be seen from Table 3 a weight ratio between dye IIIa and dye IVb of about 2 or more offers the lowest increase of the viscosity at a coating pH value of 4.5. It is clear that lower amounts of gelatin are leading to a lower increase in viscosity if the coating pH is lowered.

It has been established further that by manufacturing storage dispersions by neutralisation of alkaline solutions of these two dyes in gelatin, the ratio by weight of said dyes is important too.

Example 5

In an "in vitro" experiment the viscosity has been determined from a microprecipitation dispersion of dye-IVa or dye-IVb in the presence of dyes-IIIa, -IIIb and -IVc. Each coating solution of 1000 grams was comprising an amount of gelatin of 40 grams, having moderate viscosity. Amounts of dyestuff are given in grams in Table 4A, said amounts being added as an alkaline solution of 20% for dye-IIIa; 5% for dye-IIIb; 4% for dye-IVa; 1% for dye-IVb and 1% for dye-IVc. Viscosities in mPas after acidifying to a pH value of 5.5; 5.0 and 4.5 are given in Table 4B.

Table 4A

	D	E	F	G	H
dye-IVa	2	2	-	-	2
dye-IVb	-	-	2	2	-
dye-IIIc	4.46	-	4.46	-	-
dye-IIIb	-	-	-	-	6.40
dye-IIIa	-	6.40	-	6.40	-

Table 4B

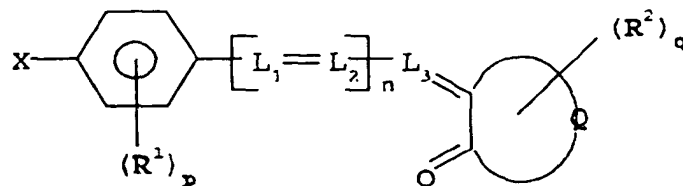
to pH	D	E	F	G	H
5.5	23	6	24	6	6
5.0	80	5.5	***	6.5	6
4.5	***	5	***	7.5	5

The same influence on the viscosity of a coating solution is obtained with dye-IVa in combination with dye-IIIb as in combination with dye-IIIa.

There is also the same positive reaction for the combination of dye-IIIa with dye-IVb as can be concluded from Table 4B. pH values were adjusted with citric acid. As can be concluded from Table 4 the viscosity in the presence of dye-IVc is too high.

Claims

1. Photographic material comprising a support and on at least one side thereof at least one light-sensitive silver halide emulsion layer characterised in that said material comprises at least one hydrophilic colloid layer, comprising a dispersion of at least two dyes: at least one dye being a merostyryl dye and the at least one other dye being an oxonol dye, wherein both dyes are soluble at a pH value above 8.0 and insoluble at a pH value below 6.0, and wherein at least said oxonol dye is in the form of a microprecipitated dispersion.
2. Photographic material according to claim 1, wherein the said merostyryl dye is represented by the general formula (I)



(I)

wherein

n represents 0 or 1;

each of p and q independently represents 0, 1 or 2;

Q represents the atoms necessary to form an acidic nucleus;

each of R¹ and R² independently represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, COOR³, NHCOR⁴ or NHSO₂R⁵ with R³ representing hydrogen or substituted or unsubstituted alkyl, each of R⁴ and R⁵ independently representing substituted or unsubstituted alkyl, or substituted or unsubstituted aryl,

X represents OR⁶, SR⁶ or NR⁷R⁸, wherein

R⁶ represents H, substituted or unsubstituted alkyl, substituted or unsubstituted aryl and

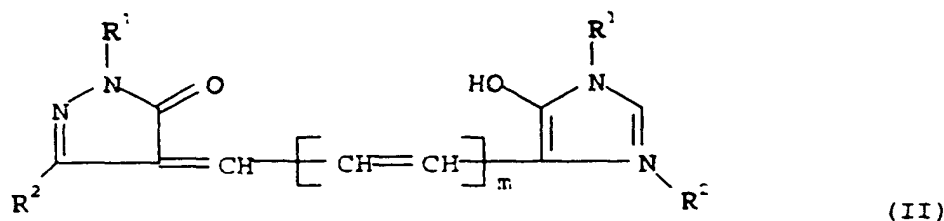
each of R⁷ and R⁸ which may be the same or different represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl or the necessary atoms to form a ring together with the N-atom to which they are attached and the C-atom of the phenylene ring in ortho position with respect to said N-atom; R⁷ and R⁸ together may also represent the necessary atoms to form a ring with the N-atom to which they are attached;

L₁, L₂, L₃ represent substituted or unsubstituted methine with the proviso that, if substituted, at least one of L₁, L₂ or L₃ must be substituted by -CONR⁹R¹⁰; -CON(R¹¹)-; -COOR⁹; -CN;

R⁹ and R¹⁰ which may be the same or different represent hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl,

wherein R¹¹ represents atoms to form a ring with an atom of Q, defined hereinbefore; and wherein at least one of R¹ to R¹¹ contains an ionizable group;

and wherein the said oxonol dye is represented by the general formula (II),



wherein

m= 0, 1 or 2;

R¹ and R² has the same meaning as in formula (I),

and at least one of R¹ and R² in formula (II) has an ionizable group.

3. Photographic material according to claim 2, wherein in the formula (I) of the said merostyryl dye the acidic nucleus is a 3-pyrazolidine-1-one, barbituric acid, thiobarbituric acid, rhodanine, hydantoin, oxazolidindione, thio-oxazolidindione, or an isoxazolinone.

4. Photographic material according to any of claims 1 to 3 wherein the absorption spectrum of the said dispersion of at least two dyes is in the region from 370 to 700 nm and wherein the amount per sq.m. of the merostyryl dye(s) corresponding to the formula (I) is from 0.1 to 0.3 g, and wherein the amount per sq.m. of the oxonol dye(s) is from 0.09 to 0.11 g.

5. Photographic material according to any of claims 1 to 4, wherein said material is an X-ray material or a material for micrography.

6. Method of processing a photographic material according to any of claims 1 to 5, comprising the steps of developing, fixing, rinsing and drying, within a total processing cycle of less than 60 seconds.

7. Method of preparing a photographic material according to any of claims 1 to 3 comprising the steps of microprecipitating at least one oxonol dye by acidifying an alkaline solution in which said at least one oxonol dye is dissolved and adding the said microprecipitated oxonol dye(s) together with at least one merostyryl dye to a hydrophilic colloid coating solution followed by coating said solution on at least one side of the support of said photographic material.

8. Method according to claim 7 comprising the steps of adding at least one oxonol dye to a hydrophilic colloid coating which contains a merostyryl dye in dispersed form, microprecipitating the oxonol dye(s) by acidifying the said coating solution and coating said solution on at least one side of the support of said photographic material.
- 5 9. Method according to claim 7 wherein the said oxonol dye(s) after microprecipitation is (are) added to an acidic hydrophilic colloid coating solution which contains a merostyryl dye in dispersed form followed by coating said solution on at least one side of the support of said photographic material.
- 10 10. Method according to any of claims 7 to 9, wherein the said merostyryl dye(s) is (are) present in dispersed form by a microprecipitation technique by the step of acidifying an aqueous alkaline solution of the said dye(s).
11. Method of preparing a photographic material according to any of claims 1 to 3 comprising the steps of preparing a dispersion wherein at least one merostyryl dye and at least one oxonol dye are microprecipitated apart or together, before or after addition to a hydrophilic colloid coating solution respectively by acidifying alkaline aqueous solutions of dye(s) or alkaline hydrophilic colloid coating solutions of said dye(s) followed by coating the acidified coating solution on at least one side of the support of said photographic material.
- 15 12. Method according to any of claims 7 to 11, wherein the said hydrophilic colloid is gelatin or silica sol.
- 20 13. Method according to any of claims 7 to 12, wherein the said acidifying proceeds by the addition of citric acid.

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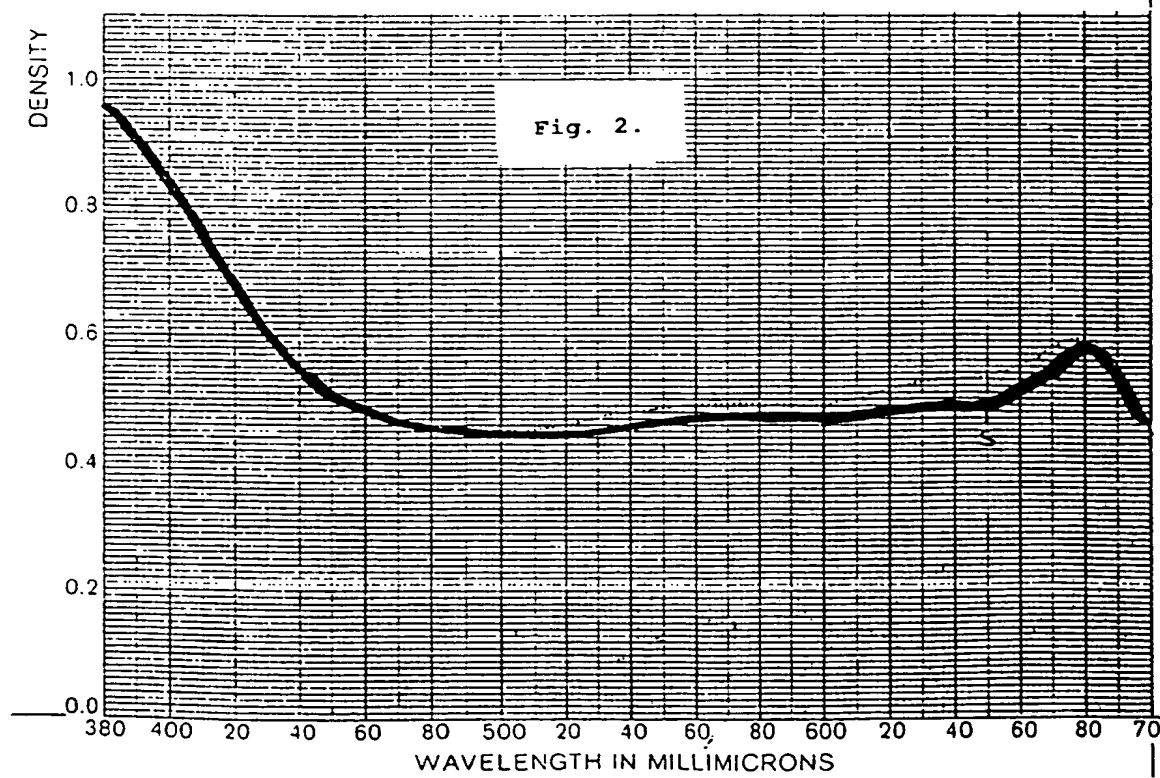
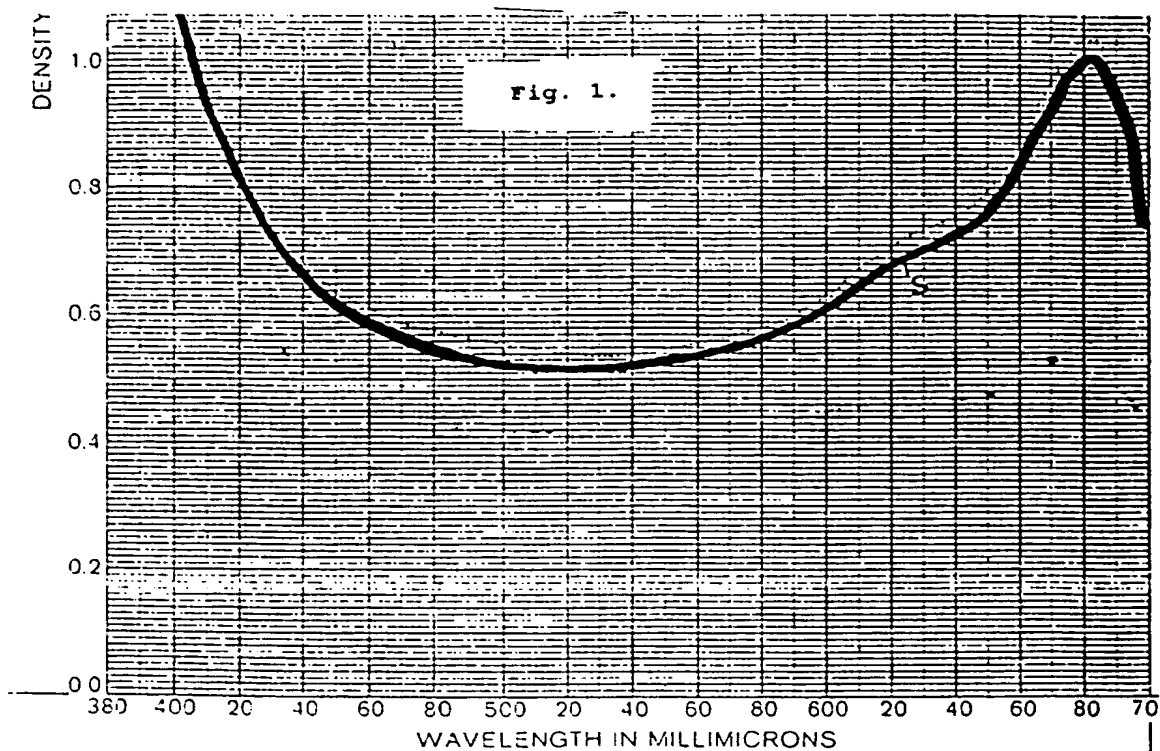
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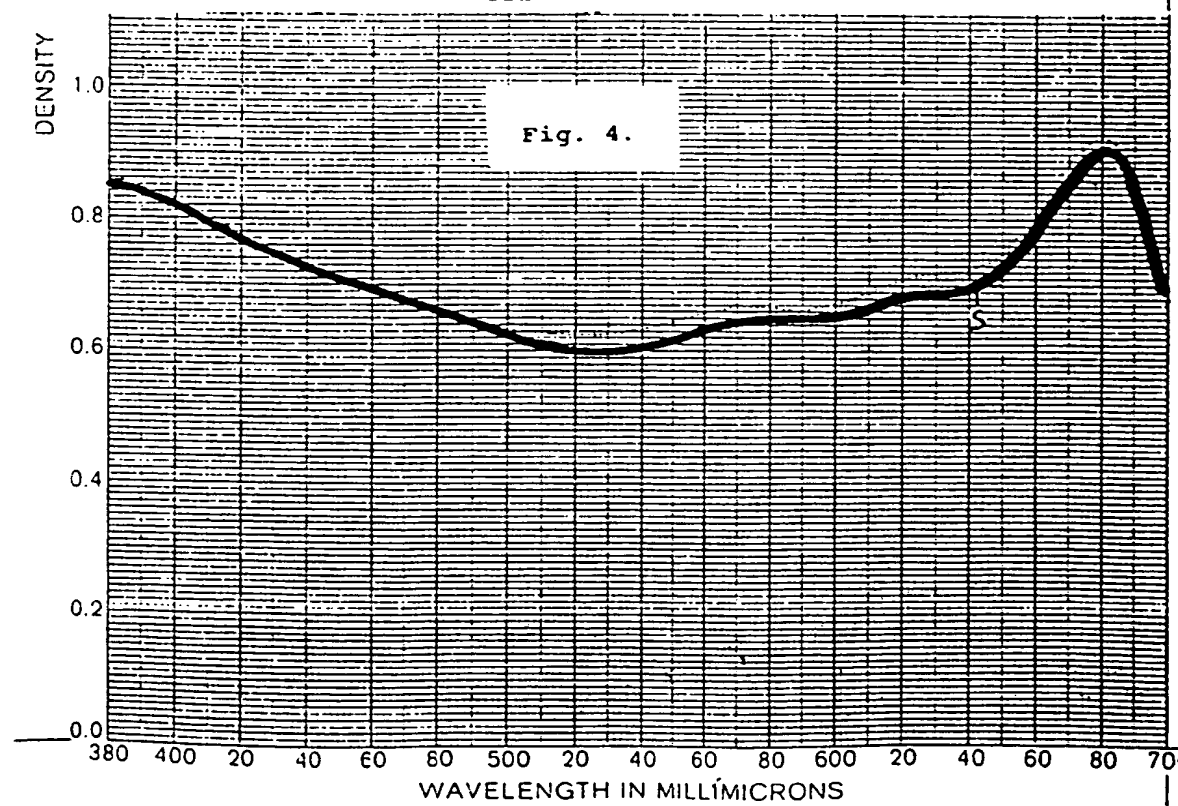
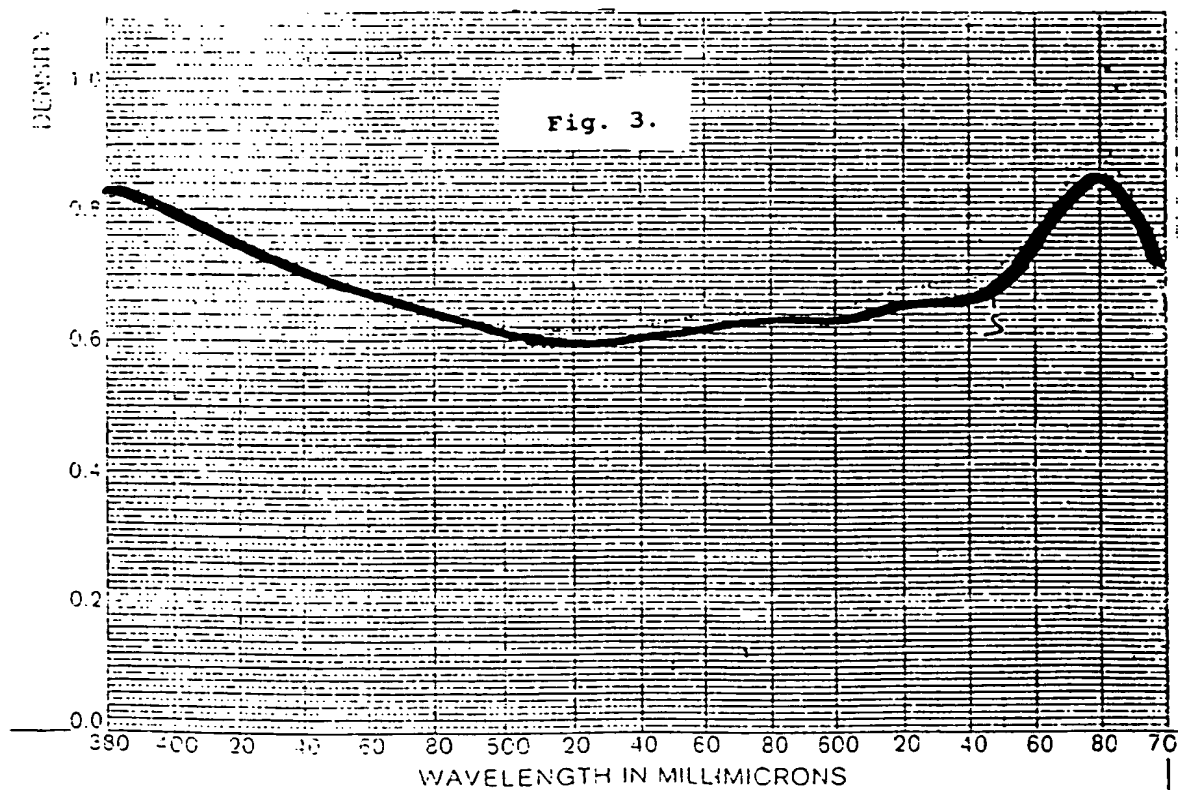
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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 3367

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	EP-A-0 554 834 (FUJI) * page 12; example I1 * * page 22, line 5 - line 11 * * page 23, line 45 - page 24, line 19 * * page 36, line 9 - line 32 * * page 40, line 16 - line 27 * ---	1-6 7-12	G03C1/83 G03C1/005
D,Y A	EP-A-0 549 489 (KODAK) * page 3, line 40 - line 54 * * page 45; example VII130 * * page 47; example VII141 * * page 75, line 7 - line 8 * * page 75, line 16 - line 18 * * page 75, line 31 - line 33 * ---	7-12 13	
D,Y	EP-A-0 587 229 (AGFA-GEVAERT) * page 7, line 19 - line 23 * * page 9, line 10 - line 31; claims 1-9 * -----	7-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 February 1996	Examiner Magrizos, S
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